

# Correlates in Groundwater Quality Parameters and Textural Classes of Soils in a Peri-industrial District of the Nigerian Delta Region

Dike Henry Ogbuagu\*, John Didacus Njoku, Atulegwu Patrick Uzoije, Joseph Ikechukwu Nwachukwu, Tochi Ezechi Ebe

Department of Environmental Technology, Federal University of Technology, PMB 1526, Owerri, Nigeria

\* E-mail of the corresponding author: [henrydike2002@yahoo.com](mailto:henrydike2002@yahoo.com)

## Abstract

This study investigated the physicochemical status of groundwaters of the oil-rich Ekakpamre community in Ughelli, Nigeria. Ten borehole water samples located about 1 km apart and soil samples around them were collected and analyzed by standard methods. Clay, sand and silt compositions in overlaying soils appeared to influence the DO ( $r=-0.999$ ), TPH & toluene ( $r=0.998$ , each), and  $K^+$  ion ( $r=-0.999$ ) levels in groundwaters at  $P<0.05$ . Three PCs which accounted for 100% variability in the original 27 variables formed the extraction solution and were most correlated with Cr (0.995), Pb (0.989) and  $PO_4^{2-}$  ions (0.947). Though the high compositions of clay ( $72.67 \pm 2.33\%$ ) and low compositions of sand ( $24.33 \pm 2.60\%$ ) in the study indicates slight possibility of migration of surface pollutants to aquifers, the exceedances of Pb and Cd levels over regulatory limits portends public health hazards to consumers of groundwaters in the area.

**Keywords:** Physiochemical status, Groundwater, Peri-industrial District, Niger Delta, Water contamination, Textural compositions

## 1. Introduction

Groundwater contamination in industrializing regions can result from such sources as leakages from landfill, effluents, tank and pipeline leakages, oilfield and agricultural sources, as well as saltwater intrusions (Olobaniyi and Owoyemi, 2006). It may also be from spills, surface discharges in the form of hydrocarbons in/around groundwater tables, or from stockpiles in industrial, construction or agricultural sites. Other likely sources include contamination from cesspools, septic tanks, and interchange through wells.

The study location in the Niger Delta Region (NDR) of Nigeria thrives in oil and gas deposits, and exploration and exploitation activities have been on for several decades now. It is known that oil and gas activities could contribute solid, liquid and gaseous contaminants to the environment and that these toxicants could infiltrate the soil profile and contaminate aquifers (Sharma *et al.*, 2004 and Zektser *et al.*, 2005; Ogbuagu *et al.*, 2011). The problems of groundwater contamination include outbreaks of water-borne diseases, as well as unsuitability of water for both agricultural and industrial uses.

Beside the oil exploration and exploitation activities, there are several other industries in the region that could contribute varying quantities of contaminants to the underground water resource. Ogbuagu *et al.* (2011) and

Okoli *et al.* (2011) have reported low water tables and varying infiltration rates of soils in the region, even as Abam (2001) had reported incidences of saline water intrusion into groundwater aquifers in the NDR, especially in proximate Rivers and Bayelsa States. Other studies in the region by Olobaniyi and Owoyemi (2006) and Ayotamuno and Kogbara (2007) have demonstrated that there are rising levels of  $K^+$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $HCO_3^-$ ,  $Cl^-$ , turbidity, and hydrocarbons in Warri, Ekpan, Edjeba, Ughelli, Kwali, Ibusa, and Asaba in Delta State, and Onne, Port Harcourt, Ndoni, Degema, Oyigbo, Etche, and Bonny in Rivers State. Other scholars have observed similar trends in other Niger Delta states of Bayelsa, and Akwa Ibom States (Oteri, 1984; Edet, 2004; Okolie *et al.*, 2005; Ekundayo, 2006; Okagbue, 1989; Olobaniyi *et al.*, 2007; Ophori *et al.*, 2007; Nwidu *et al.*, 2008).

In another study, Ekundayo (2006) reported that the Niger Delta groundwater protective soil layer consisted of inorganic clays, sandy-clay and sandy-silt mixtures in Brass Island of Bayelsa State, thus making aquifers in the area vulnerable to leakage and susceptible to pollution and saline water intrusion. The study by Ayotamuno and Kogbara (2007) revealed that groundwater at Onne experienced an increase in total dissolved solids of 15–2900 mg/L in two years. Hydrocarbon content (oil and grease) level was as high as 71mg/l as against 1.8mg/l recorded 17 years ago. Of the groundwater aquifers of the area, those of Ughelli are among the least investigated with focus on pollution, even as the town thrives in oil and gas, as well as ancillary anthropogenic activities. This study thus attempts to close this gap.

## 2 Materials and Methods

### 2.1. Study Area

Ekakpamre Community is located in Ughelli town, Delta State of Nigeria between Latitude  $5^\circ 52'N$  and Longitude  $5^\circ 58'E$  (Fig. 1). The climate of the area is humid tropical and typifies the rainforest zone of the equatorial region, with average precipitation of about 2800mm. Mean ambient temperature is  $28^\circ C$ , with relative humidity of about 88%. Wet season lasts between March–November, with a short dry season lasting the rest of the year (SPDC, 2002). The soil types include red to yellowish podzols overlying loose sand, with elevation of about 15–19m above mean sea level. The lithofacies includes channels and point bar, backswamp and the hydro-lithological characteristics includes fine to medium-coarse grained point bar sands and clayey backswamp deposits (NDES, 2000). The sands form the major aquifers in the area, while the clays form the aquitards. The water table in the area varies seasonally, as water table declines during the dry season. Generally, the water table is closer to the surface, and within a range of about 8–12m below the ground surface, depending on the season and closeness to the swampy area.

Oil exploration and exploitation operations have been ongoing for over 40 years in the area, even as the major activities of local inhabitants include peasant farming, hunting, petty trading/business and artisanal labour. The major source of water of the inhabitants is groundwater, which is abstracted for several domestic, agricultural, and industrial purposes.

### 2.2. Field sampling

The research, which was conducted in the last quarter of 2010 utilized four boreholes within Ekakpamre

community. The boreholes were chosen at about 1 km apart and designated BH 1, BH 2, BH 3, BH 4, BH 5, BH 6, BH 7, BH 8, BH 9, and control. The direction of groundwater flow was determined from the boreholes and water table map of the area (Abam, 2004).

At each sampling location, *in situ* measurements for pH, temperature, conductivity and dissolved oxygen (DO) were made in triplicates with a HORIBA U-10 Water Quality Checker that had been calibrated with standard phthalate autocalibration fluid. Total dissolved solids (TDS) was also determined electrometrically *in situ* with HACH Conductivity Meter (Model CO 150) with an inbuilt automatic TDS monitor.

At each borehole, 500mL sample bottles were pre-rinsed with the water sample before final collections. Samples for heavy metal analysis were collected in 1 litre sample bottle and fixed with 3ml of Analar grade concentrated trioxonitrate (V) acid ( $\text{HNO}_3$ ). Samples for PAHs, TPH and MAHs analyses were collected in 1 litre bottles and fixed with 5ml Analar grade concentrated tetraoxosulphate (VI) acid ( $\text{H}_2\text{SO}_4$ ). All samples were collected in triplicates, stored in iced chest and subsequently transferred to the laboratory. Triplicate soil samples were also collected with stainless soil auger at 0-15cm depths around the 3 boreholes, composited and transferred to the laboratory in labeled polythene bags as recommended by Aremu *et al.*, (2010).

### **2.3. Laboratory Analysis**

TPH, PAH and the MAH contents were determined with a gas chromatograph that was coupled with the flame ionization detector (GC-FID), while soil textures were classified according to the Bougoucouc Hydrometer method (Day, 1965). Trace elements concentrations were determined with the atomic absorption spectrophotometer according to APHA (1998).

### **2.4. Statistical Analysis**

With the use of the Statistical Package for Social Science (SPSS<sup>®</sup>) Version 17.0, descriptive statistics and Pearson correlation coefficients ( $r$ ) of the physicochemical parameters were computed. The principal components analysis (PCA) was used to remove redundant (highly correlated) variables from the data file and replacing the entire data file with a smaller number of uncorrelated variables.

## **3. Results and Discussion**

### **3.1. Physicochemical characteristics of groundwater sources**

Narrow variations were generally observed in the physicochemical parameters of groundwater samples measured. This indicates similarity in the community's aquifers with respect to physicochemical attributes. pH, total suspended and dissolved solids (TSS and TDS) varied between 6.50 and 6.80 ( $6.60 \pm 0.07$ ), 4.20 and 13.00 ( $8.83 \pm 1.99$ ) mg/L, and 16.20 and 25.20 ( $21.35 \pm 2.10$ ) mg/L, respectively (Table 1). Dissolved oxygen (DO), 5 days biological oxygen demand ( $\text{BOD}_5$ ) and TPH contents varied from 4.00-4.34 ( $4.15 \pm 0.07$ ), 1.33-3.96 ( $3.19 \pm 0.62$ ), and 0.005-0.010 ( $0.007 \pm 0.001$ ) mg/L, with ranges of 0.34, 2.63 and 0.005, respectively. Chloride, nitrate, sulphate and phosphate ions varied from 4.36-6.67 ( $6.09 \pm 0.58$ ), 0.10-0.68 ( $0.43 \pm 0.12$ ), 0.004-0.008 ( $0.006 \pm 0.00$ ), and 0.008-0.600 ( $0.157 \pm 0.148$ ) mg/L, respectively. Their ranges were 2.31, 0.58, 0.004 and 0.592, respectively. Carbonate ion ( $\text{HCO}_3^-$ ) and the cations-  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$

varied between 8.64 and 12.69 ( $10.70 \pm 1.15$ ), 1.23 and 4.10 ( $2.64 \pm 0.66$ ), 0.50 and 0.94 ( $0.70 \pm 0.11$ ), and 0.11 and 1.00 ( $0.57 \pm 0.18$ ) mg/L, with ranges of 4.05, 2.87, 0.44 and 0.89, respectively.

The trace metals- Fe, Pb, Zn and Cu varied from 0.05-0.16 ( $0.11 \pm 0.03$ ), 0.005-0.009 ( $0.007 \pm 0.001$ ), 0.008-0.010 ( $0.010 \pm 0.001$ ), and 0.008-0.030 ( $0.017 \pm 0.005$ )  $\mu\text{g/L}$ , respectively. Their ranges were 0.11, 0.004, 0.002 and 0.022, respectively. Cr and Cd varied from 0.004-0.008 ( $0.006 \pm 0.001$ ) and 0.005-0.009 ( $0.008 \pm 0.001$ )  $\mu\text{g/L}$ , with ranges of 0.004, each.

The polynuclear aromatic hydrocarbons (PAHs) varied between 0.01 and 0.03 ( $0.02 \pm 0.01$ )  $\mu\text{g/L}$ , with a range of 0.02, while the mononuclear aromatics (benzene, toluene, ethyl benzene and xylene) varied from 0.004-0.008 ( $0.006 \pm 0.001$ ), 0.002-0.005 ( $0.004 \pm 0.001$ ), 0.002-0.003 ( $0.003 \pm 0.000$ ), and 0.004-0.008 ( $0.006 \pm 0.001$ )  $\mu\text{g/L}$ , respectively. Their ranges were 0.003, 0.003, 0.001 and 0.004, respectively.

Of the parameters measured, mean Pb (0.007 $\mu\text{g/L}$ ) and Cd (0.008 $\mu\text{g/L}$ ) concentrations were above the recommended 0.01 and 0.003  $\mu\text{g/L}$  maximum permissible limits for drinking water by the World Health Organization (WHO, 2004). Metals occur naturally and become incorporated into water bodies. Some, such as mercury, copper, selenium, and zinc are essential metabolic components in low concentrations. Elevated concentrations can have negative consequences for both wildlife and humans. Anthropogenic activities could however, increase concentrations of these metals to above natural levels. The release of trace metals to the surrounding water is largely a function of pH, oxidation-reduction state, and organic matter content of the water (and the same is also true for nutrient and organic compounds) (UNEP GEMS, 2006). The high concentrations of Pb and Cd in this study could pose serious threat to human health, not only through the drinking of the water, but also through its use in the preparation of foods.

The low TDS in this study corresponds with low anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{2-}$  and  $\text{HCO}_3^-$ ) and cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , and the trace metals), in the water sample, as well as the freshwater status (absence of salinity) of the aquifers. Water with a TDS above 1,500-2,600 mg/L is generally considered problematic for even irrigation use on crops with low or medium salt tolerance (RUC, 2003).

The pH range in this study was less than 8, indicating that the dissolved carbonates exist almost entirely as  $\text{HCO}_3^-$  ion forms (Freeze and Cherry, 1979). The pH of water is important because it is closely linked to biological productivity. According to the UNEP GEMS (2006), although the tolerance of individual species varies, pH values between 6.5 and 8.5 usually indicate good water quality and this range accommodates the present study.

### **3.2. Principal components analysis (PCA)**

The communalities were all high, indicating that the extracted components represent the variables in groundwater well. The Varimax extraction method used extracted eigenvalues greater than 1. This resulted in the first 3 PCs forming the extraction solution. The cumulative % column of the Extraction Sums of Squared Loadings (Table 2) shows that the extracted components explained exactly 100% of the variability in the original 27 physicochemical variables measured in groundwaters. This indicates that no loss of

information on variability of the parameters would be lost with the use of these PCs alone. The first PC alone explained 62.76% variability, while the least variability of 12.04% was explained by the third PC. The rotation (Table 3) maintained the cumulative % of variation explained by the extraction components, but that variation is now spread more evenly over the components.

The scree plot (Fig. 2) represents the eigenvalues of each component in the initial solution, with the extracted components on the steep slope, while the components that contributed nothing to the solution are on the flat slope. The scatterplot matrix of the extracted component scores (Fig. 3) reveal that the PCs (Factors) were all normally distributed in space.

The rotated component matrix revealed that the first component was most highly correlated with Cr ions (0.995), the second with Pb ions (0.989) and the third with  $\text{PO}_4^{2-}$  ions (0.947). This makes these parameters chief pollutants in the aquifers sampled, as, by implication, their removal from these sources eliminates current pollution outcomes.

### 3.3. Textural classification of soils

Of the textural classes identified, silt had the narrowest range of 2.00 %; varying from 2.00-4.00 ( $3.00 \pm 0.58$ ) % (Table 4). However, the other classes- clay and sand varied from 69.00-77.00 ( $72.67 \pm 2.33$ ) and 20.00-29.00 ( $24.33 \pm 2.60$ ) %, with ranges of 8.00 and 9.00, respectively.

The ability of rocks and soils in any given drainage basin to buffer the acidity of water is related to the residence time of water in the soil as well as the levels of calcium carbonate, bicarbonate, and silicate minerals (Friedl *et al.*, 2004; Wetzel and Likens, 2000). Alkaline compounds in water such as bicarbonates, carbonates, and hydroxides remove hydrogen ions and lower the acidity of the water (i.e. increases pH) (UNEP GEMS, 2006). This must have been responsible for the observed slight acidity in this study.

The ionic composition of groundwater is governed by exchanges with the underlying geology of the area. Human activities within the area also influence the ionic composition, by altering discharge regime and transport of particulate matter across the landscape, and by changing the chemical composition of surface runoff of solutes (Wetzel, 2001).  $\text{Ca}^{2+}$  concentrations in this study were higher than  $\text{K}^+$ , an observation also made by Wetzel (2001) at global average level. The narrow ranges of the ionic composition of the groundwater sources indicate stability, as they are not significantly exposed and influenced by such metabolic activities as surface waters.

The low sand composition (<70%), in this study and high clay composition ( $72.67\% \pm 2.33$ ) would deter pollutants and leachates from surface origins from permeating aquifers in the region. This observation is in consonance with other works conducted in the Niger Delta areas of Nigeria (RSMENR, 2002; Agbogidi *et al.*, 2006; Don-Pedro, 2009; Hart *et al.*, 2005) and indicates that the Niger Delta geology does not greatly make groundwater aquifers susceptible to surface contaminations.

However, the presence and levels of the mononuclear and polynuclear aromatic hydrocarbons (MAHs & PAHs) in the groundwaters seem to have deferred this barrier and thus, constitutes public health hazards to local consumers. Authors have implicated these group of pollutants as mutagens and possible carcinogens to man (Evans, 1977; ATSDR, 1995. Cerna, 1996; Ogbuagu *et al.*, 2011; Okoli *et al.*, 2011).

### **3.4. Interactions of the physicochemical attributes of groundwater with textural classes**

Clay correlated negatively with DO ( $r=-0.999$ ), sand correlated positively with TPH and toluene ( $r=0.998$ , each) and silt correlated negatively with  $K^+$  ( $r=-0.999$ ) at  $P<0.05$  (Table 5). This indicates that while overlaying clay and silt compositions appeared to discourage oxygen and K ion contents, respectively in the aquifers, sand composition rather encouraged the seepages of both the aliphatic and aromatic hydrocarbons from surface/overlaying origins. Endowed with petroleum hydrocarbon deposits, Ekakpamre community houses some of the oil prospecting and exploration companies whose activities, as well as those of ancillary services could contribute petroleum pollution in the environment, even above natural levels. This becomes an issue of environmental concern as there could be future serious contaminations of the aquifers, even though current levels were below regulatory permissible limits.

### **4. Conclusions**

There were narrow variations in the physicochemical characteristics of groundwater sources in the current study, indicating similarity in the aquifers of the region. With the exception of Pb and Cd, the other parameters were below the World Health Organization's maximum permissible limits for drinking water. Though the levels of the petroleum hydrocarbons, including the mono- and poly-nuclear aromatic hydrocarbons, were within allowable limits by regulatory agency, increasing future inputs could portend heavy pollutions in the aquifers. The three principal pollutants in the aquifers of the study area were trace elements (Cr and Pb) and  $PO_4^{3-}$  ions only. Though the textural classes of soils of the study area revealed high clay and low sand compositions, indicating difficulty in permeation of surface contaminants to the aquifers, there exist statistical evidence that petroleum contaminants in them could increase on long-term basis.

Groundwater sources of the community should be treated for Pb and Cd pollutants, using the extraction, treatment and re-injection (ETR) technology; recirculating well technology (RWT) and natural attenuation methods, as the case may be.

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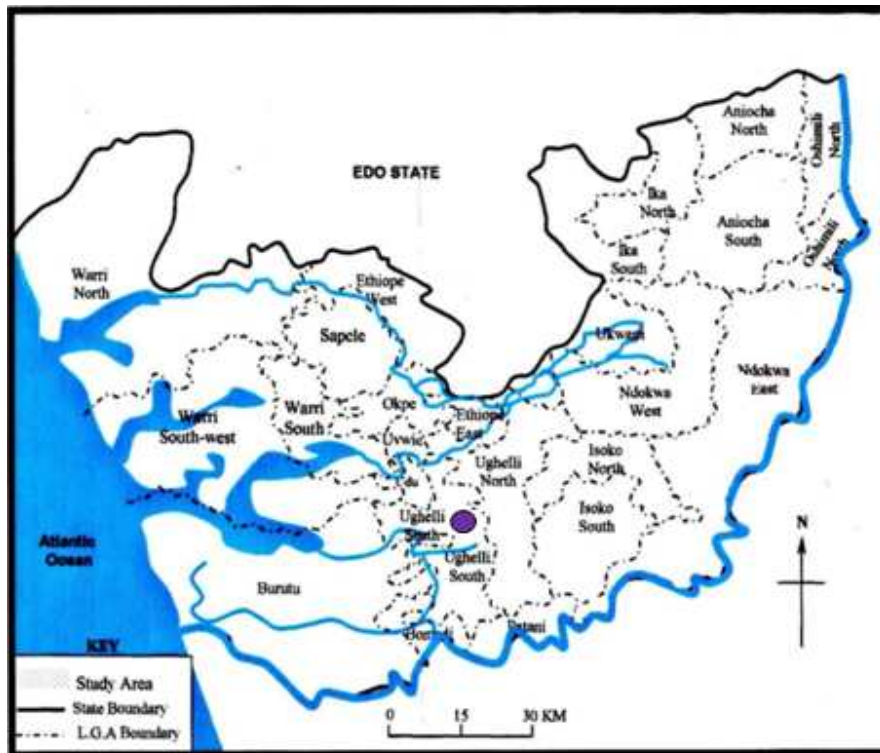
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Source: Ministry of Lands and Survey and Urban Development, Asaba, 2002.

Fig. 1. Location map of Delta State showing the study Area

### Scree Plot

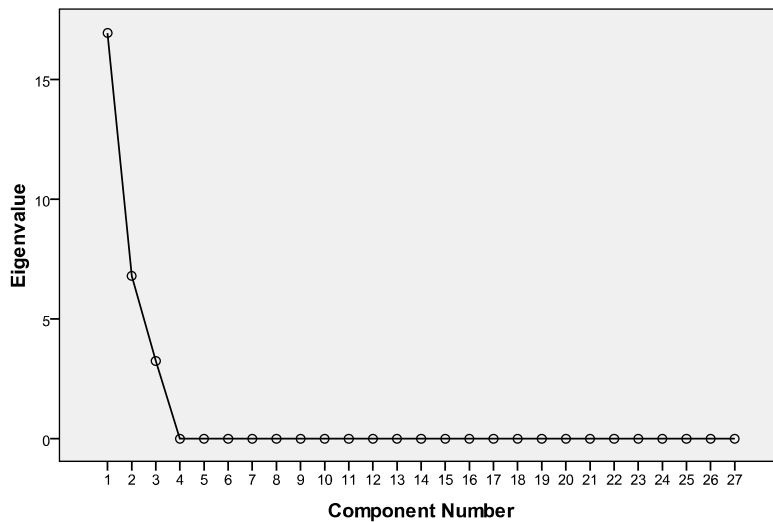


Fig. 2. Scree plot of eigenvalue of components in initial solution

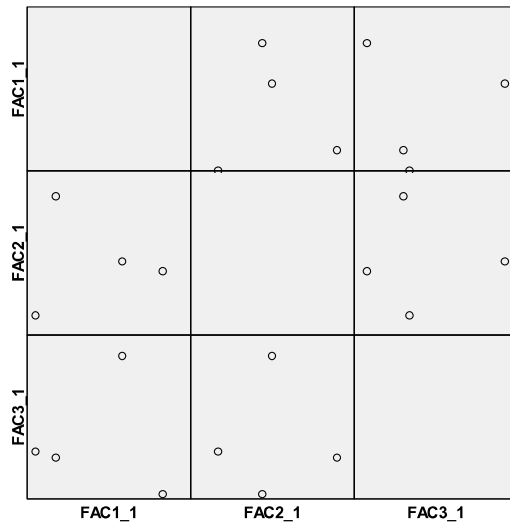


Fig. 3. Scatterplot matrix of component scores

Table 1. Levels of physicochemical parameters in groundwaters of Ekakpamre community

Parameters	Minimum	Maximum	Range	Mean	SE	WHO (2004)
pH	6.50	6.80	0.30	6.60	0.07	6.5-8.5
TSS (mg/L)	4.20	13.00	8.80	8.83	1.99	-
TDS (mg/L)	16.20	25.20	9.00	21.35	2.10	1000
DO (mg/L)	4.00	4.34	0.34	4.15	0.07	-
BOD (mg/L)	1.33	3.96	2.63	3.19	0.62	-
TPH (mg/L)	0.005	0.010	0.005	0.007	0.001	-
Cl <sup>-</sup> (mg/L)	4.36	6.67	2.31	6.09	0.58	250
NO <sub>3</sub> <sup>-</sup> (mg/L)	0.10	0.68	0.58	0.43	0.12	10
SO <sub>4</sub> <sup>2-</sup> (mg/L)	0.004	0.008	0.004	0.006	0.00	400
PO <sub>4</sub> <sup>2-</sup> (mg/L)	0.008	0.600	0.592	0.157	0.148	-
HCO <sub>3</sub> <sup>-</sup> (mg/L)	8.64	12.69	4.05	10.70	1.15	-
Na <sup>+</sup> (µg/L)	1.23	4.10	2.87	2.64	0.66	200
Ca <sup>2+</sup> (µg/L)	0.50	0.94	0.44	0.70	0.11	200
K <sup>+</sup> (µg/L)	0.11	1.00	0.89	0.57	0.18	-
Fe (µg/L)	0.05	0.16	0.11	0.11	0.03	-
Pb (µg/L)	0.005	0.009	0.004	0.007	0.001	0.01
Zn (µg/L)	0.008	0.010	0.002	0.010	0.001	3.00
Cu (µg/L)	0.008	0.030	0.022	0.017	0.005	2.00
Cr (µg/L)	0.004	0.008	0.004	0.006	0.001	0.05

<b>Cd (µg/L)</b>	<b>0.005</b>	<b>0.009</b>	<b>0.004</b>	<b>0.008</b>	<b>0.001</b>	<b>0.003</b>
<b>PAHs (µg/L)</b>	<b>0.01</b>	<b>0.03</b>	<b>0.02</b>	<b>0.02</b>	<b>0.01</b>	<b>0.7</b>
<b>Benzene (µg/L)</b>	<b>0.004</b>	<b>0.008</b>	<b>0.003</b>	<b>0.006</b>	<b>0.001</b>	<b>10</b>
<b>Toluene (µg/L)</b>	<b>0.002</b>	<b>0.005</b>	<b>0.003</b>	<b>0.004</b>	<b>0.001</b>	<b>700</b>
<b>Ethylbenzene(µg/L)</b>	<b>0.002</b>	<b>0.003</b>	<b>0.001</b>	<b>0.003</b>	<b>0.000</b>	<b>300</b>
<b>Xylene (µg/L)</b>	<b>0.004</b>	<b>0.008</b>	<b>0.004</b>	<b>0.006</b>	<b>0.001</b>	<b>500</b>

SE = standard error of mean, TPH = total petroleum hydrocarbons, WHO = World Health Organization

Table 2. Extraction Sums of Squared Loadings of components in groundwaters

<b>Components</b>	<b>Total</b>	<b>% of Variance</b>	<b>Cumulative %</b>
<b>1</b>	<b>16.946</b>	<b>62.763</b>	<b>62.763</b>
<b>2</b>	<b>6.803</b>	<b>25.197</b>	<b>87.960</b>
<b>3</b>	<b>3.251</b>	<b>12.040</b>	<b>100.000</b>

Table 3. Rotation Sums of Squared Loadings of components in groundwaters

<b>Components</b>	<b>Total</b>	<b>% of Variance</b>	<b>Cumulative %</b>
<b>1</b>	<b>13.807</b>	<b>51.138</b>	<b>51.138</b>
<b>2</b>	<b>8.327</b>	<b>30.840</b>	<b>81.978</b>
<b>3</b>	<b>4.866</b>	<b>18.022</b>	<b>100.000</b>

Table 4: Textural classes of soils of Ekakpamre Community

<b>Parameters (%)</b>	<b>Minimum</b>	<b>Maximum</b>	<b>Range</b>	<b>Mean</b>	<b>SE</b>
<b>Clay</b>	<b>69.00</b>	<b>77.00</b>	<b>8.00</b>	<b>72.67</b>	<b>2.33</b>
<b>Sand</b>	<b>20.00</b>	<b>29.00</b>	<b>9.00</b>	<b>24.33</b>	<b>2.60</b>
<b>Silt</b>	<b>2.00</b>	<b>4.00</b>	<b>2.00</b>	<b>3.00</b>	<b>0.58</b>

SE = standard error of mean

Table 5: Correlations (r) between physicochemical variables in groundwaters and textural classes of soils of Ekakpamre community

Parameters	Clay	Sand	Silt
pH	-0.143	-0.064	0.866
TSS	0.442	-0.248	-0.669
TDS	0.292	-0.089	-0.780
DO	-0.999*	0.968	-0.327
BOD	0.597	-0.749	0.967
TPH	0.990	0.998*	0.000
Cl <sup>-</sup>	0.000	0.000	0.000
NO <sub>3</sub> <sup>-</sup>	-0.017	-0.189	0.922
SO <sub>4</sub> <sup>2-</sup>	0.459	-0.266	-0.655
PO <sub>4</sub> <sup>2-</sup>	0.927	-0.831	-0.003
HCO <sub>3</sub> <sup>-</sup>	0.143	0.064	-0.866
Na <sup>+</sup>	0.471	-0.279	-0.644
Ca <sup>2+</sup>	-0.753	0.873	-0.890
K <sup>+</sup>	-0.401	0.581	-0.999*
Fe	0.011	0.195	-0.924
Pb	-0.143	-0.064	0.866
Zn	0.143	0.064	-0.866
Cu	0.577	-0.396	-0.545
Cr	-0.189	0.387	-0.982
Cd	0.786	-0.896	0.866
PAHs	-0.619	0.444	0.500
Benzene	-0.484	0.654	-0.992
Toluene	0.990	0.998*	0.500
Ethyl benzene	-0.189	0.387	-0.982
Xylene	-0.166	0.366	-0.977

\*=significant at P<0.05 (95% confidence interval)

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